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Effect of Al doping on the structural and optical properties of SnO_2 thin films elaborated by sol-gel technique

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Abstract
In this study, the influence of increasing of the Al concentration on the structural and optical properties of SnO_2 thin films were investigated. Pure and aluminum-doped SnO_2 thin films were prepared by sol–gel deposition method on glass and Si (100) substrates at room temperature and then annealed at 550°C in air. The obtained films are characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), and UV–Vis spectrophotometry techniques. A single-phase rutile polycrystalline structure is revealed by XRD. The AFM analysis show that the surface morphology changes with Al concentration. The un-doped and Al-doped SnO_2 thin films are transparent (86% optical transmittance) in the near UV-Vis, and the optical band gap is influenced by Al doping level.

Keywords: Al-doped SnO_2; sol–gel; XRD; AFM; UV-Vis.

1. Introduction

Tin oxide (SnO_2) is one of the most important transparent conductive oxide (TCO) materials, used in numerous applications in modern technologies, such as solar cells [1] as conductive transparent electrode, [2] in transistors, [3] in varistors, [4] and in sensors [5]. This is a result of its attractive properties of a wide band gap semiconductor (gap in the range 3.5–4.0 eV [6]), high transparency in the visible range (90%) and high reflectivity in the infrared energy range [7].

Different techniques were used to prepare SnO_2 or doped SnO_2 thin films, i.e., spray pyrolysis, [8-9] sol–gel process, [10-12] chemical vapor deposition, [13,14] sputtering, [15,16] pulsed-laser deposition [17].

In this work, Sol–Gel Dip Coating (SGDC) was employed to obtain pure and aluminum (Al) doped SnO_2 thin films at room temperature on glass and Si (100) substrates. The structural and optical properties of the elaborated Al-doped SnO_2 thin films were studied and the Al effects were investigated.

2. Experimental details

The aluminum-doped tin dioxide sols were prepared by dissolving of $SnCl_2$.$5H_2O$ in absolute ethanol. To achieve Al doping, aluminum nitrate was added to the precursor solution. The doping concentration varied from 0–6 at. %. The solution was stirred at 60°C for 2 h in a closed container for the homogenous mixing of the solution, i.e. until the solid materials dissolved. The thin films were deposited by the dip-coating technique on glass and Si (100) substrates, which had been cleaned ultrasonically in acetone. The clean glass and Si (100) substrates were dipped vertically and carefully into the sol for a short time, and withdrawn from the bath at withdrawal speeds in the range from 1mm/s to 10 mm/s. This was followed by drying and then sintering of the films at 550°C for 2 h. To obtain with higher thickness films, the sequence of dipping, drying and then dipping again was performed a number of times. However, sintering was done only after the final dipping. The thickness of the films increased, almost linearly [18], with the number of dipping.

The structural properties of the deposited films were studied by means of grazing incidence X-ray diffraction (GIXRD) using CuKα radiation (λ = 1.54056 Å) from Bruker-AXS.D8 diffractometer. The surface morphology was observed by atomic force microscopy (AFM) Pacific Nanotechnology. The optical transmittance was measured on a Shimadzu 3101 PC UV-visible spectrophotometer.

3. Results and discussion

3.1. Structure and surface morphology

The X-ray diffraction patterns of the pure and Al doped SnO_2 thin films deposited on glass and Si (100) substrate with different Al concentrations were are shown in Fig 1. In the case of the thin films deposited on glass substrate (Fig 1-a), the spectra presented an amorphous structure. This was due to the effect of the substrate nature on the structural properties of thin films.

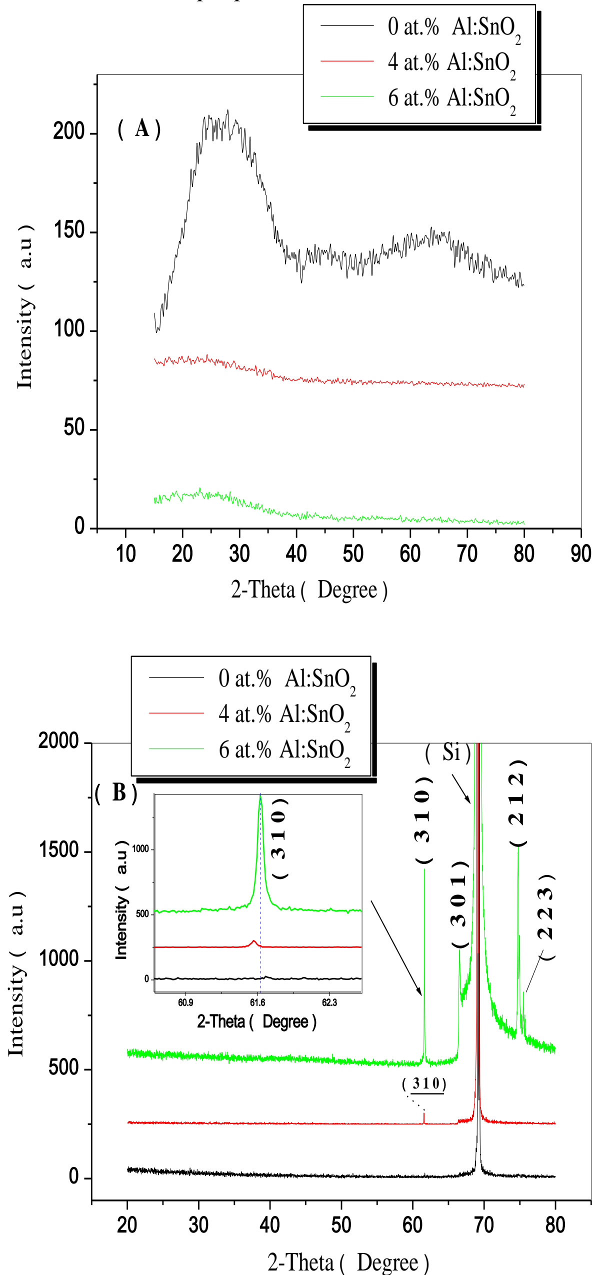

Figure 1: X-ray diffraction patterns of Al doped SnO_2

However the spectra of pure and Al:SnO_2 deposited on Si (100) substrate (Fig 1-b) revealed the polycrystalline nature of the films with tetragonal structure. In addition to the peak of Si(100) substrate , the existence of four peaks were observed with 61,62°; 66,52°; 74,80° and 75,67° corresponding to the plans (310); (301); (212) and (223) respectively, of the polycrystalline rutile SnO_2 patterns [19]. The peak intensity observed at (310) plane was found to increase gradually with the increase of Al concentration. These peaks were slightly moved to the high values of the Bragg diffraction angle theta (θ) when the Al concentration increased. This suggested the presence of mechanical compressive strains in the Al:SnO_2 lattice. In addition, no peak relating to Al or Al_2O_3 was observed in XRD spectra.

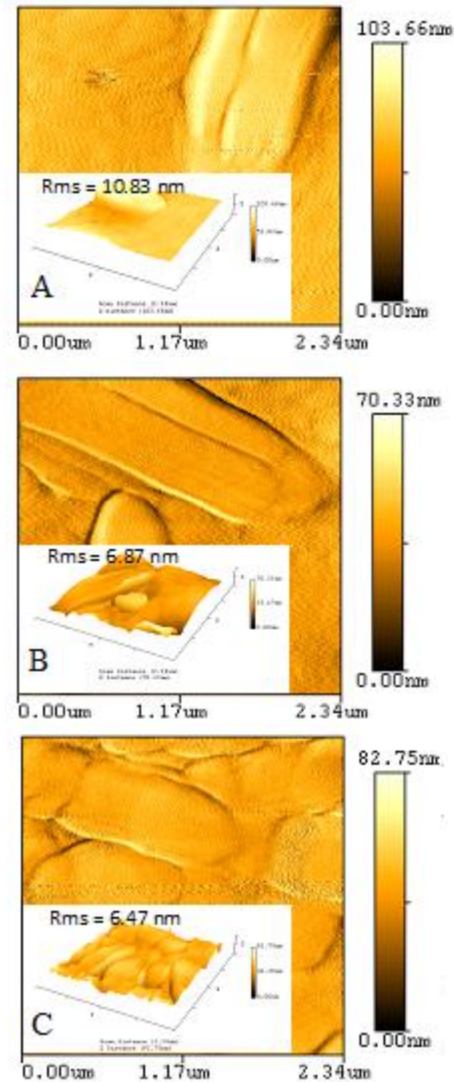

Figure 2: AFM images of the Al:SnO_2 films (a) 0 at.% Al:SnO_2, (b) 4 at.% Al:SnO_2 and (c) 6 at. % Al:SnO_2.

It was established that the micro-roughness of thin films played a vital role for developing optical coatings especially in the UV region [20] for applications such as lithographic uses [21]. To characterize an optical surface (coatings) the root-mean-square (RMS) roughness was normally used. The RMS roughness described not only the light scattering but also gave an idea about the quality of the surface. The surface morphology of the Al: SnO_2 films deposited onto Si(100) substrate was shown in Fig 2 with 2D and 3D

modes. It could be inferred from these AFM images that smoother films could be obtained by Al doping.

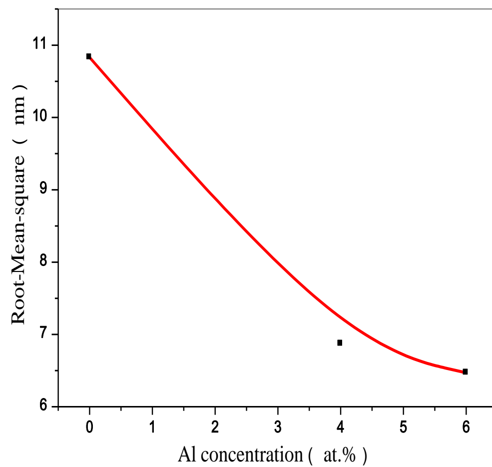

Figure 3 : Root-Mean-Square (RMS) Vs Al concentration.

The plot of RMS surface roughness values computed for the Al: SnO_2 thin films on Si(100) substrate as a function of aluminum concentration was shown in Fig. 3. The plotted curve showed clearly that roughness RMS of the SnO_2 layers doped with Al was lower than for the un-doped SnO_2 thin films. These results were of great importance in the photovoltaic uses. Moreover, the AFM images let observe morphology of the surface structural dense and compact.

3.2. Optical transmittance

Optical characteristics of Al:SnO_2 thin films versus Al atomic content were measured using UV-Vis transmittance spectra. Fig 4 showed the plot of transmittance of Al :SnO_2 thin films as a function of the light wavelength.

From the Fig 4 it was easy to observe that the behavior of transmittance for the un-doped and Al doped films was almost similar in the wavelength range of 350–800 nm and the values of the optical transmittance increased with increasing of Al concentration. The average percentage of transmittance of all the samples was varied between 85% and 87% in the visible region. The transmittance was found to increase gradually when the aluminum concentration increased above 2 at.%. The increase in transmittance with the increase in doping concentration might be attributed to the decrease in the both cluster size and surface roughness of the films. The registered transmittance values were higher compared with earlier reported values [22], attesting the high quality of the prepared Al:SnO_2 thin films. Also, it was easy to notice a slight red shift of the absorption edge with increasing Al doping (Fig 4).

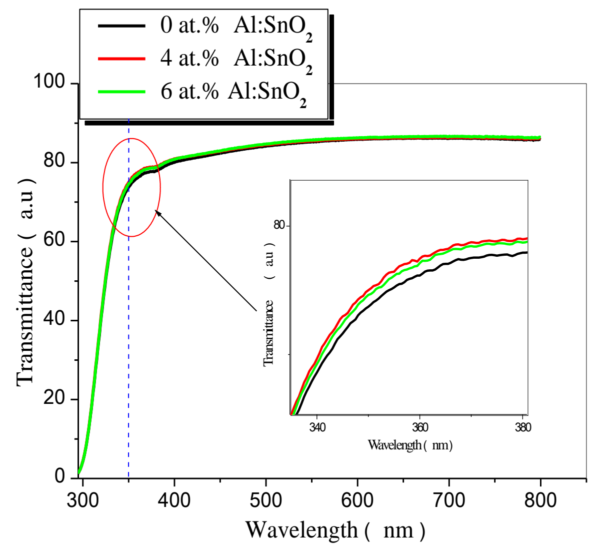

Figure 4 : Optical transmittance of un-doped and Al-doped SnO_2 thin films as a function of wavelength.

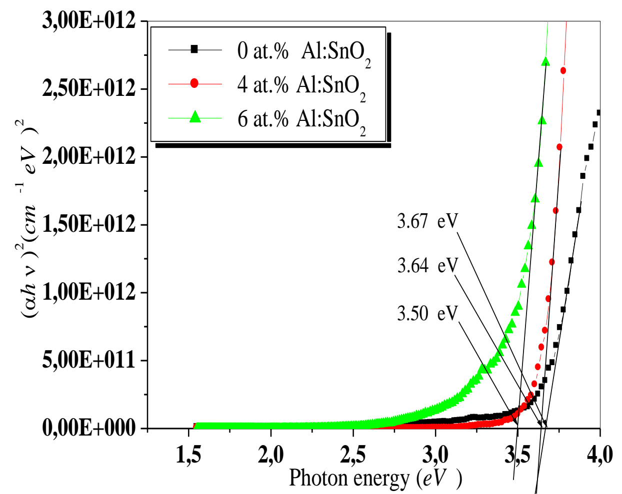

Figure 5 : Typical variation of $(\alpha h\nu)^2$ as a function of photon energy.

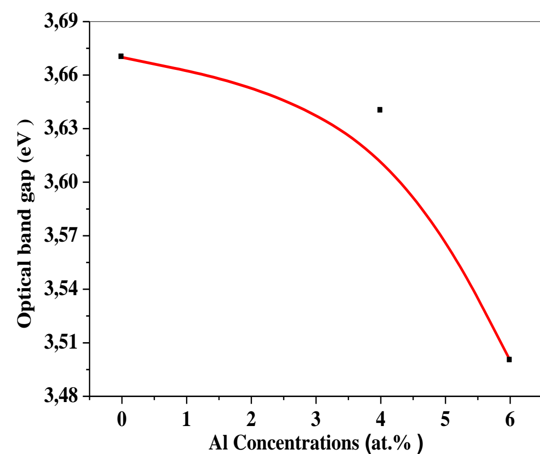

Figure 6: Variation of the band gap energy (Eg) of Al-doped SnO_2 thin films as a function of Al concentration.

The optical band gap (Eg) of the films was evaluated by conventional method by extrapolating the straight line portion of the $(\alpha h\upsilon)^2$ vs. hυ curve to α=0. The band gap energy deduced from Fig 5 was plotted in Fig 6 as a function of Al concentration. The calculated band gap for 0 at.%, 4 at.% and 6 at% of Al doped SnO_2 are 3.67, 3.64, and 3.50eV respectively. The curve (Fig 6) showed clearly that the optical energy gap decreased with increasing Al doping. These Eg values were almost in agreement with those of P.S. Patil and al. [23].

Indeed, the incorporation of aluminum atoms as doping into the SnO_2 lattice led to a red shift of Eg. The observed shift was attributed to an increase of the free carriers concentration in Al:SnO_2 films. Consequently, the photoabsorption performance of the Al:SnO_2 thin films as TCO used in photoelectrical devices was improved.

4. Conclusion

Aluminum doped SnO_2 thin films have been fabricated by Sol Gel Dip Coating method on Si(100) and on glass substrates. The XRD analysis showed that the Al:SnO_2 films deposited on monocrystalline Si(100) crystallized in the rutile structure with an improvement of the crystallinity with the aluminum incorporation. However, the study revealed an amorphous structure in the case of Al:SnO_2 thin films deposited on glass. The AFM observations showed a decrease of surface roughness (RMS) with increasing Al concentration. Also, the optical UV-Vis transmittance measurements showed that the transparency of the obtained SnO_2 thin films increased with increasing Al content. The optical absorption edges of all films lay in the range of 300 to 400 nm and the deduced energy band gap values varied from 3.50 to 3.67eV.

References

[1] C.Y. Kim, D.H. Riu, Thin Solid Films, 519 (2011) 3081–3085.

[2] R. E. Presley, C.L. Munsee, C.H. Park, D. Hong , J.F. Wager, D.A. Keszler, J. Phys. D: Appl. Phys., 37 (2004) 2810–2813.

[3] L.L.Chi, J. K.Chou, W.Y. Chung, , T. P. Sun, S.K.Hsiung, Mater. Chem. Phys. 63 (2000) 19–23.

[4] M. R.Cassia-Santos, V. C. Sousa, M. M.Oliveir, F. R. Sensato, W. K.Bacelar J. W. Gomes, Mater. Chem. Phys. 90 (2005) 1–9.

[5] X. Du, Y. Du, S. M. George, J. Phys. Chem. A, 112 (2008) 9211–9219.

[6] A. F. Khan, M. Mehmood, M. Aslam, M. Ashraf, Applied Surface Science 256 (2010) 2252–2258.

[7] M. Batzill, U. Diebold, Prog. Surf. Sci. 79 (2005) 47–154.

[8] R. S. Niranjan, K. R. Patil, R. S. Sainkar, K. Vijayamohanan, S. Mulla, Mater. Chem. Phys. 84 (2004) 37–45.

[9] R. L. Mishra, K.M. Sheo, S. G. Prakash, J. Ovonic. Res, 5(4) (2009) 77-85.

[10] G. Ramanathan, R.X. John, K.R. Murali, Elixir Thin Film Tech, 50 (2012) 10588.

[11] M. T. Kesim, C. Durucan, Thin Solid Films, 545 (2013) 56–63.

[12] S. Mohammadi, H. Abdizadeh, M.R.Golobostanfard, Ceramics International, 39 (2013) 4391–4398.

[13] M. Maleki, S. M. Rozati, Bull. Mater. Sci., 36(2) (2013) 217-221.

[14] D.W. Sheel, J.M. Gaskell, Thin Solid Films, 520 (2011) 1242–1245.

[15] V. Kumar, A. Jain, D. Pratap, D.C. Agarwal, I. Sulania, V. V. Siva Kumar, A. Tripathi, S.Varma , R.S. Chauhan, Adv. Mat. Lett., 4(6) (2013) 428-432.

[16] L. M. A. Camacho, C. J. R. Galeana, G. A. Esparza, C. Sánchez, C. M. Julien, Superficies y Vacío, 26(3) (2013) 95 -99 .

[17] H. Kim, R.C.Y. Auyeung, A. Piqué, Thin Solid Films, 516 (2008) 5052–5056.

[18] S. K. Tripathy , P. V. Rajeswari , B. P. Hota, The African Review of Physics, 7 (2012) 265–268

[19] Joint Committee on Powder Diffraction Standards (JCPDS); International Centre for Diffraction Data: Newtown Square, PA, USA, (1997).

[20] A. Duparre, Handbook of Optical Properties, vol. 1, CRC Press, (1995), pp. 273–304.

[21] M. Senthilkumar, N.K. Sahoo, S. Thakur, R.B. Tokas, Appl. Surf. Sci. 245 (2005) 114.

[22] S. Sriram, A. Thayumanavan, Int. Journal of ChemTech Research. 5 (2013) 2204 -2209.

[23] P.S. Patil, R.K. Kawar, T. Seth, D.P. Amalnerkar, P.S. Chigare, Ceramics International. 29 (2003) 725-734.